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STANDARD OPERATING PROCEDURE FOR THE ANALYSIS OF
MERCURY IN SEDIMENT AND SOLIDS
METHOD 245.5 (AUTOMATED H₂SO₄/HNO₃ PREDIGESTION & COLD VAPOR)

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1. **SCOPE AND APPLICATION:**

- 1.1 This method determines total mercury in sediment and solids. It can be used to analyze samples when SW-846 is recommended.
- 1.2 Total mercury determined by this method consists of both inorganic and organic forms of mercury.
- 1.3 Method detection limit (MDL) with precision and accuracy studies must be performed and approved before this standard operating procedure (SOP) may be used for analysis, and repeated for any major revisions. These studies evaluate whether the reporting limits and calibration standard concentrations are appropriate, among other things. Determine the MDL when results below the reporting limit are requested by a customer or annually whichever is less often. The method detection limit based on 0.1 g of a soil sample that is 100% solid is 0.03 mg/Kg.
- 1.4 The normal working range of this method is 0.2 µg/g to 2.0 µg/g. The reporting limit based on 0.1 g of a soil sample that is 100% solid is 0.1 mg/Kg. The reporting limit will be the lowest value reported unless specifically requested by a customer.
- 1.5 Single laboratory uncertainty for this method determined following CRL.SOP GEN006 (statistical method, page 13) at the 95% confidence interval using the laboratory control sample (LCS) at 1.5 µg/L was found to have a mean of 98.5% (1.48µg/L) and an uncertainty of 4.1% (0.06µg/L). The uncertainty may be greater near the reporting limits and much larger near the detection limits.

2. **SUMMARY OF METHOD:**

- 2.1 A weighed portion of the sample is digested in a fully automated water bath for 2 minutes at 95°C in aqua regia followed by oxidation with potassium permanganate (KMnO₄) reagent. The potassium permanganate (KMnO₄) reagent is added in excess.
 - 2.1.1 Hydroxylamine hydrochloride (NH₂OH•HCl) reagent is automatically added to the sample in the water bath after the oxidation step to reduce the excess potassium permanganate (KMnO₄) reagent.
- 2.2 Mercury in the digested sample is reduced to elemental form during the automated spectrophotometric analysis step using stannous chloride (SnCl₂) reagent.
 - 2.2.1 The resulting elemental mercury is purged from the sample analysis

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stream into the spectrophotometer cell.

- 2.3 The absorption of the reduced mercury vapor is measured at 253.7 nm. This is proportional to the concentration of mercury in the sample.

3. **DEFINITIONS:**

- 3.1 CALIBRATION BLANK (CB) -- A volume of reagent water fortified with the same matrix as the calibration standards, but without the analytes, internal standards, or surrogate analytes.
- 3.1.1 INITIAL CALIBRATION BLANK (ICB) --A calibration blank analyzed at the beginning of the analysis run to demonstrate that the instrument is capable of acceptable performance.
- 3.1.2 CONTINUING CALIBRATION BLANK (CCB) -- A calibration blank analyzed in the course of the analysis run to demonstrate that the instrument is capable of continuous acceptable performance.
- 3.2 CALIBRATION STANDARD (CAL) -- A solution prepared from the primary standard solution or stock standard solutions and the internal standards and surrogate analytes. The calibration standards solutions are used to calibrate the instrument response with respect to analyte concentration.
- 3.2.1 CAL_n -- n (where n = 1, 2, etc) indicate the calibration levels.
- 3.3 CONTROL STANDARD (CS) -- A solution prepared from the primary standard solutions or stock standard solutions and the internal standards and surrogate analytes. Control standard is prepared in the same manner as the calibration standard. The control standard solutions are used to demonstrate that the instrument is capable of acceptable performance.
- 3.3.1 INITIAL CALIBRATION VERIFICATION - CONTROL STANDARD (ICV-CS) -- A control standard analyzed at the beginning of the analysis run to demonstrate that the instrument is capable of acceptable performance.
- 3.3.2 CONTINUING CALIBRATION VERIFICATION - CONTROL STANDARD (CCV-CS) -- A control standard analyzed in the course of the analysis run to demonstrate that the initial calibration determined remains valid throughout the course of the analytical run.
- 3.4 INSTRUMENT PERFORMANCE CHECK SOLUTION (IPC) -- A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the performance of the instrument system with respect

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to a defined set of criteria.

- 3.5 LABORATORY FORTIFIED BLANK (LFB) -- An aliquot of reagent water or other blank matrices to which known quantities of method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.
- 3.6 LABORATORY FORTIFIED SAMPLE MATRIX (LFM) -- An aliquot of an environmental sample to which known quantities of method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.
- 3.7 LABORATORY REAGENT BLANK (LRB) -- An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or apparatus.
- 3.8 LINEAR CALIBRATION RANGE (LCR) -- The concentration range over which the instrument response is linear.
- 3.9 MATERIAL SAFETY DATA SHEET (MSDS) -- Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.
- 3.10 METHOD DETECTION LIMIT (MDL) - The minimum concentrations of analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.
- 3.11 QUALITY CONTROL SAMPLE (QCS) - A solution of method analytes of known concentrations that is used to fortify an aliquot of reagent blank (LRB) or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.
- 3.12 STOCK STANDARD SOLUTION (SSS) - A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.
- 3.13 LABORATORY DUPLICATE (LD1 and LD2) - Two aliquots of the same

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sample taken in the laboratory and analyzed separately with identical procedures. Analyses of a number of LD1 and LD2 indicates precision associated with the laboratory procedures, but not with sample collection, preservation, or storage procedures.

- 3.14 FIELD DUPLICATE (FD1 and FD2) - Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout the field and laboratory procedures. Analyses of a number of FD1 and FD2 indicates the precision associated with the sample collection, preservation and storage, but not with the laboratory procedures.

4. SAFETY AND WASTE HANDLING:

- 4.1 Mercury vapor will be generated by this procedure. This vapor is toxic. Proper precautions must be taken to avoid exposure to it.
- 4.2 Sample digestion for mercury analysis must be done in a properly ventilated area.
- 4.2.1 Vent all products of vapor generation into an exhaust hood.
- 4.3 All unused working standards, reagents, and sample aliquots must be discarded into an orange labeled waste container.
- 4.4 Waste generated during sample analysis must be handled in the following manner.
- 4.4.1 The liquid waste generated at the gas-liquid separator must be drained into an orange labeled waste container.
- 4.4.2 The mercury vapor purged from the sample analysis stream into the spectrophotometer cell must be trapped by passing it through an absorbing media containing activated carbon or vented into an exhaust hood.
- 4.5 All other wastes produced in performing this method must be disposed of according to the Central Regional Laboratory Safety, Health, and Environmental Compliance Manual.

5. INTERFERENCES:

- 5.1 No potential interferences were studied with this method.
- 5.2 The following interferences are known to exist.
- 5.2.1 Sulfide interference is eliminated by the addition of potassium permanganate (KMnO₄) reagent.

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5.2.2 Chloride interference is removed by the addition of hydroxylamine hydrochloride ($\text{NH}_2\text{OH} \cdot \text{HCl}$) reagent.

5.2.3 Volatile organic compounds which absorb at 253.7 nm interfere with this method.

5.2.3.1 When this interference is suspected, analyze the affected sample with and without the stannous chloride (SnCl_2) reagents and compare their results.

5.2.4 Copper interference has been reported to have no effects on the recoveries of mercury from spiked samples at concentrations as high as 10 mg Cu/L in water samples.

6. **APPARATUS:**

6.1 DIGESTION APPARATUS:

6.1.1 Water bath (VWR Part# 62687-069 or equivalent).

6.1.2 Hot plate (Thermolyne - Cimarec 3 or equivalent).

6.1.3 Thermometer (Non mercury - 10 to 200 °C).

6.1.4 ***Consumables;***

6.1.4.1 Centrifuge tube racks.

6.1.4.2 30 X 120 mm disposable centrifuge tubes.

6.1.5 Oxford pipettes (5 ± 0.05 mL and 10 ± 0.1 mL)

6.1.6 Eppendorf pipettes (200 μL (accuracy $\pm 0.6\%$), 500 μL (accuracy $\pm 0.6\%$, 1000 μL (accuracy $\pm 0.6\%$), and 1000 μL adjustable (accuracy 100 $\mu\text{L} \pm 3\%$, 1000 $\mu\text{L} \pm 0.6\%$))

6.2 ANALYTICAL APPARATUS:

6.2.1 P.S.A Millennium mercury atomic absorption analyzer system.

6.2.2 An auto sampler (PSA model 20.400 or equivalent).

6.2.3 A data system.

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6.2.4 Consumables

6.2.4.1 Auto sampler cups.

6.2.4.2 Compressed gas (Argon, pre-purified or Ultra High Purity)

6.3 Plastic containers - High density polyethylene (HDPE) or equivalent.

6.4 Stirring Plates and stir bars (teflon coated).

6.5 Volumetric flasks (Class A, 100 mL, 500 mL, 1000 mL, and 2000 mL).

7. **REAGENTS:**

7.1 Reagent water : De-Ionized water (ASTM type II water or equivalent).

7.2 Sulfuric Acid (H_2SO_4), concentrated - ACS reagent grade.

7.3 Nitric Acid (HNO_3), concentrated - ACS reagent grade.

7.4 Hydrochloric acid (HCl), concentrated - ACS reagent grade.

7.5 Potassium permanganate (KMnO_4) - ACS reagent grade.

7.6 Potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) - ACS reagent grade.

7.7 Hydroxylamine hydrochloride ($\text{NH}_2\text{OH} \cdot \text{HCl}$) - ACS reagent grade.

7.8 Sodium chloride (NaCl) - ACS reagent grade.

7.9 Stannous chloride (SnCl_2) - ACS reagent grade.

7.10 Mercuric chloride (HgCl_2) - ACS reagent grade.

7.11 Methyl mercury (II) chloride (CH_3HgCl) - ACS reagent grade.

7.12 All reagents and standard preparations must be properly documented. The prepared solutions are to be stored in appropriately labeled containers.

7.12.1 Label reagent containers as follows;

PARAMETER:	(MERCURY)
IDENTITY:	(Stannous Chloride Reagent)
DATE OF PREPARATION:	(mm/dd/yyyy)

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EXPIRATION DATE: (mm/dd/yyyy)
LIMS ID
INITIALS OF PREPARER: (F.A.)

7.12.2 Label standard containers as follows;

PARAMETER: (MERCURY)
IDENTITY: (Intermediate Calibration Standard (ICS))
CONCENTRATION: (100 µg Hg/L)
DATE OF PREPARATION: (mm/dd/yyyy)
EXPIRATION DATE: (mm/dd/yyyy)
LIMS ID
INITIALS OF PREPARER: (F.A.)

7.12.3 Commercial reagents used are pre-labeled. Mark date opened.

7.12.4 A procedure for dissolving and mixing working reagents or standards are provided in section 7.13. Use this procedure to dissolve and mix reagents or standards to be used as necessary.

7.12.5 Record and maintain reagent and standard preparations and traceability information as shown in appendix 2 on page 36 and in the log books.

7.12.6 Log all standards and reagents preparation information in LIMS.

7.12.7 Maintain certificate of analyses for all commercial standards on file.

7.12.8 For all standard prepared, record the standard source, preparation date, expiration date, LIMS ID, and the analyst initial on the standard bottles and in the quality control log book.

7.13 DISSOLVING AND MIXING REAGENT:

7.13.1 *General Instructions:*

- 7.13.1.1 All reagents and standards are prepared in volumetric flasks. Deviations are given in the specific reagent preparation section.
- 7.13.1.2 Reagents are not to be heated to dissolve unless specified in the appropriate section.
- 7.13.1.3 Mixing to dissolve solid reagents during preparation can be accomplished manually or mechanically.

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- 7.13.1.3.1 Manually by shaking and swirling to dissolve the solid reagents or mix liquid reagents.
- 7.13.1.3.2 Mechanically by using teflon coated magnetic stir bar and stirring plate.
- 7.13.1.4 It is recommended that solid reagents be dissolved mechanically. Refer to section 7.13.1.3.2.
- 7.13.1.5 When magnetic stir bars and stirring plates are used to dissolve reagents, it is necessary to follow specific procedures to place and remove a stir bar from a flask in which the reagent solution is prepared.
 - 7.13.1.5.1 Refer to section 7.13.2 to place a stir bar in the solvent and begin to dissolve solid reagent.
 - 7.13.1.5.2 Refer to section 7.13.3 to remove a stir bar from the dissolved reagent solution.
- 7.13.1.6 Liquid reagents can be mixed manually to dissolve. Refer to section 7.13.1.3.1.
- 7.13.1.7 When all reagents are dissolved, fill the flask or container to required volume. This is usually the mark if volumetric flasks were used.
- 7.13.1.8 Final mixing can be done by repeated inversion of the flask or container.

7.13.2 *Placing a teflon coated stir bar in the flask or container with solvent:*

- 7.13.2.1 Obtain a clean volumetric flask or container. The size of the flask or container is recommended under each reagent preparation section.
- 7.13.2.2 Fill the volumetric flask or container with the minimum amounts of de-ionized water or solvent suggested under the preparation section for the reagent.
- 7.13.2.3 Gently drop a teflon coated stir bar into the volumetric flask (7.13.4.2).

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- 7.13.2.4 Place the flask (section 7.14.3) on a stirring plate and begin to gently stir the de-ionized water or solvent (7.13.4.4).

7.13.3 *Dissolving solid reagents:*

- 7.13.3.1 While stirring the de-ionized water or solvent as described in section 7.13.2.4, carefully transfer the amounts of reagents required into the flask. This is obtained from the specific reagent preparation section.
- 7.13.3.2 Continue to stir the reagent solution in section 7.14.2.4. While still stirring, cautiously add more de-ionized water to the volumetric flask until it is approximately 95% full.
- 7.13.3.3 Remove the stir bar from the solution following the procedure given in section 7.13.4.

7.13.4 *Removing the stir bar from the reagent solution and filling to volume:*

- 7.13.4.1 Remove the volumetric flask or container from the stirring plate in section 7.13.3.5 and place it on a bench.
- 7.13.4.2 Place a magnetic retriever on the outside of the flask and drag or slide the stir bar out and above the solution level.
- 7.13.4.3 Rinse the stir bar with a small quantity of solvent or de-ionized water as required, into the solution.
- 7.13.4.4 Completely withdraw the stir bar from the volumetric flask.
- 7.13.4.5 Fill the volumetric flask to the mark.
- 7.13.4.6 Perform final mixing by repeated inversion.

7.13.5 *Reagent storage:*

- 7.13.5.1 Transfer the solution from section 7.13.4.5 into the recommended container storage. This is given under the individual reagent section.
- 7.13.5.2 Label the storage containers following the instruction given in section 7.12.1 or 7.12.2.

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--Preparation of Digestion Reagents

7.14 *Potassium Permanganate (KMnO₄) Reagent (5% W/V):*

- 7.14.1 Use the procedure given in section 7.12 and 7.13 as necessary to prepare and store this reagent.
- 7.14.2 Weigh 50 g of potassium permanganate (KMnO₄) reagent.
- 7.14.3 Dissolve the weighed potassium permanganate (KMnO₄) reagent (section 7.15.2) in a one liter volumetric flask containing approximately 700 mL of de-ionized water.
- 7.14.4 Dilute the solution to the one liter mark.
- 7.14.5 Filter the solution using a glass fiber filter.

NOTE: The resulting solution is dark. It is difficult to see if all the solid reagents are completely dissolved. Undissolved solid reagents cause obstruction in the syringe pump manifold.

- 7.14.6 Transfer the filtered solution into a plastic container for storage.
- 7.14.7 **Prepare this solution weekly.**

7.15 *Hydroxylamine Hydrochloride Reagent (NH₂OH•HCl):*

- 7.15.1 Use the procedure given in section 7.12 and 7.13 as necessary to prepare and store this reagent.
- 7.15.2 Separately weigh 120 g of hydroxylamine hydrochloride (NH₂OH•HCl) and 120 g of sodium chloride (NaCl) reagent.
- 7.15.3 Dissolve the weighed reagents (section 7.15.2) in a one liter volumetric flask containing approximately 500 mL of de-ionized water.
- 7.15.4 Dilute the solution to the one liter mark.
- 7.15.5 Transfer the solution into a plastic container for storage.
- 7.15.6 **Prepare this solution every three months.**

--Preparation of Analytical Reagents--

7.16 *Stannous Chloride Reagent (SnCl₂):*

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7.16.1 Use the procedure given in section 7.12 and 7.13 as necessary to prepare and store this reagent.

7.16.2 Using a graduated cylinder, measure 150 mL of de-ionized water and transfer it into a 1 liter volumetric flask.

7.16.3 Add 50 mL of concentrated hydrochloric acid (HCl) reagent to the flask (section 7.16.2).

7.16.4 Weigh 25 g of stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) reagent. Dissolve the reagent in the flask (section 7.18.3).

7.16.6 Dilute the solution to the one liter mark.

7.16.7 Filter the solution using a glass fiber filter.

7.16.8 Transfer the solution into a plastic container for storage.

7.16.9 **Prepare this solution weekly.**

7.17 ***Rinse Bank:***

7.17.1 Use the procedure given in section 7.12 and 7.13 as necessary to prepare and store this reagent.

7.17.2 Pipette 10 mL of concentrated nitric acid (HNO_3) reagent into a 2000 mL volumetric flask containing approximately 1900 mL of de-ionized water.

7.17.3 Dilute the solution to the 2000 mL mark with de-ionized water and mix properly by repeated inversion.

7.17.4 Transfer the solution into a plastic container for storage

7.17.5 **Prepare this solution monthly.**

--Preparation of Standards--

7.18 ***Stock Calibration Standard (SCS) 1.0ml = 1.0mg Hg):***

7.18.1 Commercial inorganic mercury standards containing 1000 mg Hg/L are available. Those standards can be purchased and used for the SCS.

7.18.2 The stock calibration standard (SCS) can also be prepared from mercuric chloride (HgCl_2) reagent as follows;

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- 7.18.2.1 Use the procedure given in section 7.12 and 7.13 as necessary to prepare and label this reagent. It is not necessary to use a stir bar to dissolve this reagent.
- 7.18.2.2 Weigh 0.1354 g of mercuric chloride (HgCl_2) reagent. Dissolve the reagent in a 100 mL volumetric flask containing approximately 75 mL of reagent water.
- 7.18.2.3 Add 0.5 mL of concentrated nitric acid (HNO_3) reagent to the solution (section 7.18.2.2) and continue to mix it.
- 7.18.2.4 Dilute the solution to the 100 mL mark. Mix it properly.
- 7.18.2.5 Store the solution in the volumetric flask or glass container.
- 7.18.2.6 Record the date of preparation and the analyst initials on the stock standard bottle and in the Quality Control log book.
- 7.18.2.7 **Prepare every six months.**

7.19. ***Intermediate Calibration Standard 1 (ICS-1, 1.0 mL = 10 μg Hg):***

- 7.19.1 Commercial inorganic mercury standards containing 10 mg Hg/L are available. Those standards can be purchased and used for the SCS.
- 7.19.2 If a 10 mg Hg/L stock solution is not available, prepare one from the 1000 mg Hg/L solution (7.18.1 or 7.18.2) as follows;
 - 7.19.2.1 Use the procedure given in section 7.12 and 7.13 as necessary to prepare and label this reagent.
 - 7.19.2.2 In a 100 mL volumetric flask containing approximately 40 mL of de-ionized water, pipette 0.5 mL of concentrated nitric acid (HNO_3). Mix by swirling the flask.
 - 7.19.2.3 Then pipette 1.0 mL of stock standard solution (7.19.1 or 7.19.2) into the volumetric flask (section 7.19.2.2). Swirl the flask to mix the solution.
 - 7.19.2.4 Dilute the solution to the 100 mL mark with reagent water. Mix by repeated inversion.
 - 7.19.2.5 Store the solution in the volumetric flask or glass container.

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7.19.2.6 Record the date of preparation and the analyst initials on the stock standard bottle and in the Quality Control log book.

7.19.2.7 **Prepare every six months.**

7.20 ***Intermediate Calibration Standard 2 (ICS-2, (1.0 mL = 0.1 µg Hg) ;***

7.20.1 Use the intermediate standard solution prepared in section 7.19 to make the ICS-2 solution. Prepare the ICS-2 solution as follows;

7.20.1.1 Use the procedure given in section 7.12 and 7.13 as necessary to prepare and label this reagent.

7.20.1.2 Pipette 0.5 mL of concentrated nitric acid (HNO₃) reagent into a 100 mL volumetric flask containing approximately 40 mL de-ionized water. Mix gently swirling the flask.

7.20.1.3 Then pipette 1.0 mL of intermediate standard solution (7.19.1 or 7.19.2) into the flask (section 7.20.1.2). Continue to mix the flask by swirling.

7.20.1.4 Dilute the solution to the 100 mL mark with de-ionized water. Mix it properly by repeated inversion.

7.20.2.5 Store the solution in the volumetric flask or glass container.

7.20.1.6 Record the date of preparation and the analyst initials on the stock standard bottle and in the Quality Control log book.

7.20.1.7 **Prepare this solution weekly.**

7.21 ***Working Calibration Standard (WCS):***

7.21.1 Prepare working calibration standards from the ICS-2 made in section 7.20 to cover the range of the analysis.

7.21.2 Use the procedure given in section 7.12 and 7.13 as necessary to prepare and label this reagent.

7.21.3 Make dilutions of the volumes given in Table 1 of this section.

7.21.4 Prepare each calibration standard in the following manner.

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- 7.21.4.1 Fill 100 mL volumetric flask with approximately 40 mL of reagent water.
- 7.21.4.2 Add 0.5 mL of **concentrated nitric acid (HNO₃)** reagent and mix the solution.
- 7.21.4.3 Pipette the volume of ICS-2 needed to prepare the working calibration standard. Mix it by swirling the flask.
- 7.21.4.4 Dilute the solution to the 100 mL mark with reagent water. Mix properly by repeated inversion.
- 7.21.4.5 Record the date of preparation and the analyst initials on the standard bottle.
- 7.21.4.6 Repeat steps 7.21.3.1 to 7.21.3.5 until all the working calibration standards are made.
- 7.21.4.7 Store the solution in the volumetric flask or glass container.
- 7.21.4.8 Prepare the working calibration standards daily.

TABLE 1: WORKING CALIBRATION STANDARDS

Volume of ICS-2 Diluted to 100 mL	Concentration (µg Hg/L)
0.0	0.0
0.5	0.5
1.0	1.0
1.5	1.5
2.0	2.0

7.22 Calibration Blank/Reagent Blank:

- 7.22.1 Use the procedure given in section 7.12 and 7.13 as necessary to prepare and label this reagent.
- 7.22.2 Pipette 0.5 mL of concentrated nitric acid (HNO₃) reagent into 100 mL volumetric flasks containing approximately 40 mL of de-ionized water. Mix by swirling the solution. Larger quantity can be prepared by proportional increase in reagent volumes.

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7.22.3 Dilute the solution to the 100 mL mark with reagent water. Mix properly by repeated inversion.

7.22.4 Store the solution in the volumetric flask.

7.22.5 **Prepare daily with the WCS (section 7.21).**

7.23 *Stock Control Standard solution (ScS, 1.0 mL = 1.0 mg Hg):*

7.23.1 The stock control standard (ScS) must be either purchased or prepared by someone other than the analyst.

7.23.2 Commercial inorganic mercury standards containing 1000 mg Hg/L are available. Those standards can be purchased and used for the ScS.

7.23.3 The reagent or standard used for the preparation must not be from the same source as the calibration standard.

7.23.4 Prepare the ScS from any suitable inorganic mercury compound.

7.23.4.1 Prepare the ScS in the same manner as the calibration standard.

7.23.4.2 Refer to section 7.18 for the proper preparation and documentation procedure.

7.23.5 Prepare this standard every six months.

7.24 *Intermediate Control Standard 1 (IcS-1, 1.0 mL = 10 µg Hg):*

7.24.1 Commercial standard containing 10 mg Hg/L are available. Such standards could be purchased and used.

7.24.2 If a commercial standard containing 10 mg Hg/L is not available for use, prepare one from the ScS made in section 7.23.

7.24.2.1 IcS-1 must be prepared by someone other than the analyst.

7.24.2.2 Prepare the IcS-2 solution in the same manner as the calibration standard.

7.24.2.3 Refer to section 7.21 for the proper preparation, storage, and documentation procedure.

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7.24.3 Prepare this standard every six months.

7.25 Intermediate Control Standard 2 (IcS-2, 1.0 mL = 0.1 µg Hg):

7.25.1 Use the intermediate standard solution prepared in section 7.24 to make the ICS-2 solution.

7.25.1.1 IcS-2 must be prepared by someone other than the analyst.

7.25.1.2 Prepare the IcS-2 solution in the same manner as the calibration standard.

7.25.1.3 Refer to section 7.22 for the proper preparation, storage, and documentation procedure.

7.25.1.4 **Prepare this standard weekly.**

7.26 Working Control Standard (WcS):

7.26.1 Make the WcS from IcS-2 obtained from section 7.25.

7.26.2 Prepare the WcS in the same manner as the WCS.

7.26.2.1 Refer to section 7.23 for the proper preparation, storage, and documentation procedure.

TABLE 1: WORKING CONTROL STANDARDS

Volume of IcS-2 Diluted to 100 mL	Concentration (µg Hg/L)
1.5	1.5

7.26.2.2 **Prepare this standard daily.**

--Preparation of Digestion QC--

7.27 Digestion Quality Control Standard (DQCS, 1.0 mL = 1.0 mg Hg):

7.27.1 Commercial organic mercury standards containing 1000 mg Hg/L are available. Those standards can be purchased and used.

7.27.2 The DQCS can also be prepared from methyl mercuric chloride (CH₃HgCl) reagent.

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7.27.3 This reagent requires prolonged stirring to dissolve. Follow the procedure outlined in section 7.12 and 7.13 and use a stir bar to dissolve it.

7.27.3.1 Accurately weigh 0.1252 g of methyl mercuric chloride (CH_3HgCl) reagent.

7.27.3.2 Transfer the reagent into a 100 mL volumetric flask containing a stir bar.

7.27.3.3 Wash any reagent sticking on the side of the weighing boat or container into the flask (7.27.3.2) with small quantities of de-ionized water as necessary.

7.27.3.4 Fill the flask (7.27.2.3) with approximately 75 mL of de-ionized water and begin to stir the solution.

7.27.3.5 Add 0.5 mL of concentrated nitric acid (HNO_3) reagent to the solution and continue to stir.

7.27.3.6 Stir the solution for approximately one hour. Continue to stir after one hour if necessary.

7.27.3.7 Dilute the solution to the 100 mL mark. Mix it properly.

7.27.3.8 Record the date of preparation and the analyst initials on the stock standard bottle and in the Quality Control log book.

7.27.3.9 **Prepare every six months.**

7.28. ***Intermediate Digestion Quality Control Standard (IDQCS-1, 1.0 mL = 10 μg Hg):***

7.28.1 Commercial organic mercury standards containing 10 mg Hg/L are available. Those standards can be purchased and used for the IDQCS.

7.28.2 If a commercial standard containing 10 mg Hg/L is not available for use, prepare one from the DQCS made in section 7.27.

7.28.2.1 Prepare the DQCS solution in the same manner as the ICS-1. Refer to section 7.19 for the proper preparation, storage, and documentation procedure.

7.28.3 **Prepare this standard every six months.**

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7.29 ***Intermediate Digestion Quality Control Standard 2 (IDQCS-2, 1.0 mL = 0.1 µg Hg):***

7.29.1 Use IDQCS-1 prepared in section 7.29 to make IDQCS-2.

7.29.1.1 Prepare IDQCS-2 solutions in the same manner as ICS-2. Refer to section 7.20 for the proper preparation, storage, and documentation procedure.

7.29.1.2 Prepare this standard weekly.

8. SAMPLE HANDLING AND PRESERVATION:

8.1 Samples are collected in high density polyethylene containers which meet the requirements for trace metals sample collection.

8.2 Samples are preserved by freezing or icing at the time of collection.

8.3 The holding time for mercury in sediment and solids have not been established.

8.4 Upon receipt, samples are checked for proper preservation. The customer must be notified of any problems in order to determine appropriate action.

9 QUALITY CONTROL:

9.1 Users of this method must operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, the periodic analysis of laboratory reagent blanks, fortified blanks and other laboratory solutions as continuing check on performance. The user is required to maintain performance records that define the quality of the data that are generated.

9.2 All quality control limits were reviewed on 6/23/2005. A summary of QC limits and dates of actions taken (reviewed or updated) are provided in section 11.2.5.1.

9.3 INITIAL DEMONSTRATION OF PERFORMANCE:

9.3.1 Prior to analyzing samples by this method, the following determinations and analysis must be successfully completed and documented.

9.3.1.1 Determination of the LCR.

9.3.1.2 Determination of the MDL.

9.3.1.3 Analysis of QCS.

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9.3.2 ***Determination of Linear Calibration Range (LCR):***

9.3.2.1 The LCR is established and verified prior to analysis as part of the instrument calibration procedure using the standards prepared in section 7.21, 7.22, and 7.26. See section 11.2.5.1.

9.3.3 ***Determination of the Method Detection Limit (MDL):***

9.3.3.1 Determine the MDL when results below the reporting limit are requested by a customer or annually whichever is less often. See section 11.2.5.1.

9.3.4 ***Analysis of Quality Control Sample (QCS):***

9.3.4.1 Analyze QCS quarterly or as required. Evaluate the results using the acceptance criteria provided with the QC sample.

9.3.5 Maintain all determination and analysis information in a file or logbook.

9.4 ASSESSING LABORATORY PERFORMANCE:

9.4.1 If any of the calibration verification audits or Instrument Performance Check (IPC) Solutions (ICB, CCB, ICV-CS, and CCV-CS) is out of the limit, repeat the analysis of that standard with the same aliquot or prepare a fresh aliquot and analyze. Evaluate the result using the stated limits. If the audit still failed, perform the necessary corrective action and re-calibrate the instrument. All samples following the last successful calibration audit must be re-analyzed.

9.4.2 If any of the preparation audits (LRB, LFB, LD, or LFM) is found to be out of the limit during the analysis, repeat the analysis of the failed audit using either the same aliquot or a prepare a fresh one. Evaluate the results against the stated limits.

9.4.3 If any of the failed preparation audits is still outside the limit, proceed with the rest of the analysis and evaluate the entire QC for the analysis.

9.4.4 When any or all of the preparation audits (LRB, LFB, LD, or LFM) are out of the limit, it may be necessary to re-digest all the affected batches. When it is determined that this is the case, use fresh clean glass wares. Verify that the laboratory water is of good quality, the standards are properly prepared, and all the equipments are functioning properly. Prepare fresh reagents and standards if necessary.

9.4.5 ***Laboratory Reagent Blank (LRB):***

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9.4.5.1 At least one LRB must be analyzed per preparation batch of twenty samples or less. Evaluate the result using the limit $0 \pm \text{MDL}$. See section 11.2.5.1.

9.4.5.2 If the LRB is outside the limit, verify that there is no contamination. Thoroughly clean the analytical manifold with de-ionized water. Use fresh clean glass wares. Verify that the laboratory water is of good quality. Prepare fresh reagents and standard if necessary.

9.4.6 *Laboratory Fortified Blank (LFB):*

9.4.6.1 At least one LFB must be analyzed per preparation batch of twenty samples or less.

9.4.6.2 Prepare the LFB by adding 1.0 mL of Intermediate Control Standard 2 (ICs-2) solution prepared in section 7.27 ($1.0 \text{ mL} = 0.1 \mu\text{g Hg}$) per 100 mL of LRB. This is equivalent to $1.0 \mu\text{g Hg/L}$ in 100 mL of LFB.

9.4.6.3 Evaluate the LFB as a recovery. Limit $100 \pm 13\%$. See section 11.2.5.1.

9.4.7 *Digestion Quality Control (DQC-LFB):*

9.4.7.1 Analyze a laboratory fortified blank spiked with organic mercury standard prepared at the required frequency.

9.4.7.2 Prepare the DQC by adding 1.5 mL of Intermediate Digestion Quality Control Standard (IDQCS) solution prepared in section 7.29 ($1.0 \text{ mL} = 0.1 \mu\text{g Hg}$) per 100 mL of LRB. This is equivalent to $1.5 \mu\text{g Hg/L}$ in 100 mL of DQC-LFB.

9.4.7.3 Evaluate the DQC as a recovery. Limit $100 \pm 13\%$. See section 11.2.5.1.

9.4.7.4 If commercial QC sample is used, evaluate the result using the acceptance criteria provided with the standard.

9.4.8 *Instrument Performance Check (IPC) Solution:*

Analyze ICB, CCB, ICV-CS, and CCV-CS at the required frequencies. Any failed audit requires corrective action. All samples following the last successful audit must be re-analyzed.

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9.5 ASSESSING ANALYTE RECOVERY AND DATA QUALITY:

9.5.1 *Laboratory Duplicate (LD; LD_n, n = 1 or 2);*

9.5.1.1 Samples selected for duplicate analysis are designated by the sampling organization.

9.5.1.2 If no designation is made, select at least one sample from each site for duplicate analysis or 5% of a batch if 20 or more samples are collected from a particular site.

9.5.1.2.1 The sample aliquot taken for duplicate analysis must be from the same bottle as the sample.

9.5.1.3 Analyze the sample (LD1) and duplicate (LD2).

9.5.2 Calculate the duplicate difference using the equation:

$$RPD = \frac{(LD1 - LD2)}{(LD1 + LD2)/2} \times 100\%$$

Where,

RPD = relative percent difference.

LD1 = laboratory sample duplicate, first member.

LD2 = laboratory sample duplicate, second member.

9.5.3 Evaluate the duplicate difference using the limit $RPD \pm 20\%$. See section 11.2.5.1.

9.5.3.1 If the duplicate RPD% is within the limits, no further action is required.

9.5.3.2 If the RPD% is out of the limit and results are to be reported, the Group Leader will be notified with the analyst recommendation for a final evaluation of the data.

9.5.3.3 If the RPD% is out of the limit and the sample results are close to the detection limit, calculate the absolute difference as follows;

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$$\Delta = |LD1 - LD2|$$

Where,

Δ = Absolute difference.

LD1 = laboratory sample duplicate, first member.

LD2 = laboratory sample duplicate, second member.

9.5.4 Evaluate the duplicate difference using the limit $\Delta \pm 0.2 \mu\text{g Hg/L}$ as follows. See section 11.2.5.1;

9.5.4.1 If the duplicate difference Δ is within the limits, no further action is required.

9.5.4.2 If delta exceeds $0 \pm 0.2 \mu\text{g Hg/L}$ and results are reported, the Group Leader will be notified with the analyst recommendation for a final evaluation of the data.

9.5.5 ***Laboratory Fortified Sample Matrix (LFM);***

9.5.5.1 Samples selected for matrix spike are designated by the sampling organization.

9.5.5.2 If no designation is made, select at least one sample from each site for spiking or 5% of a batch if 20 or more samples are collected from a particular site.

9.5.5.2.1 The sample aliquot taken for spiking must be from the same bottle as that used for the sample analysis.

9.5.5.3 Prepare the LFB by adding 1.0 mL of Intermediate Control Standard 2 (IcS-2) solution prepared in section 7.27 (1.0 mL = 0.1 $\mu\text{g Hg}$) per 100 mL of sample. This is equivalent to 1.0 $\mu\text{g Hg/L}$ in 100 mL of LFM.

9.5.6 Calculate the recovery using the equation:

$$R = \frac{C_s - C}{S} \times 100\%$$

Where,

R = percent recovery.

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C_s = fortified sample concentration.

C = sample background concentration.

S = Concentration equivalent of analyte added to sample.

9.5.7 Evaluate the spike recovery using the limit $100 \pm 20\%$. See section 11.2.5.1.;

9.5.7.1 Compare the calculated recovery values for information purposes to the LFM limit of $100 \pm 13\%$.

9.5.7.2 If the spike recovery exceeds $100 \pm 20\%$ and results are to be reported, the Group Leader will be notified with the analyst recommendation for a final evaluation of the data.

9.6 If any of the audits, LRB, LFB, LD, or LFM is out of the limits, it may be necessary to re-distill all the samples in the affected batch.

10. **CALIBRATION AND STANDARDIZATION:**

10.1 Refer to section 6.2 for the mercury analyzer and accessories used for this method.

10.2 ***Mercury analyzer instrument set-up:***

10.2.1 Turn on power to the Millennium AAS unit using the rear and front panel switches. Check that the power LED is illuminated.

10.2.2 Allow a minimum of 20 minutes for the mercury and background lamp to stabilize. If the lamp is not stable, allow up to one hour.

10.2.3 Turn on power to the auto sampler.

10.2.4 Turn on the Argon gas. The gas pressure should read 20 psi at the argon regulator.

10.2.5 Turn on power to the computer. Select the Millennium mercury software.

10.2.6 Follow the instrument operation procedure and software manual and check that the instrument settings are accurate.

10.2.7 Method Set-up;

10.2.7.1 Name, time, originator/Modifier

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Method title: Hg 0 – 2 ppb
 Method History: X
 Method type: Millennium Atomic Absorption
 Last Modified: DDMMYYYY
 Modified by: Initials

10.2.7.2 Method Parameters;

Unit: µg/L
 Allow Auto-Range: No
 Gain: 10
 Mode: Absorption
 Measurement Mode: Height
 Baseline Check Type: Unit
 Baseline Check Value: 5
 Filter Factor: 32
 Auto Zero: No
 Allow Negative Results: Yes
 Blank Subtraction: No

10.2.7.3 Instrument Parameters;

Delay Period (s): 15
 Analysis Period (s): 40
 Memory Period (s): 60
 Pump 1 Speed (%): 100%
 Pump 2 Speed (%): 100%
 Valve Flush: On
 Idle Action Active: No
 -Idle After: 6 minutes
 -Switch off Pump 1: No
 -Switch off Pump 2: No
 -Switch off Dryer Gas: No

Over Range Action: Default

10.3 *Preparing Calibration Standards for Analysis:*

10.3.1 Prepare a series of standards covering the desired range of analysis. For the working range of 0 to 2.0 µg Hg/L refer to section 7.21, 7.22, and 7.26.

10.4 *Entering Standard and sample Tray information:*

10.4.1 Standard and sample analysis information can be entered at any time in the Millennium mercury software 10.2.5

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10.4.2 Follow the instrument operation procedure and software manual to input standard and sample tray information for the auto sampler.

10.4.3 The following auto-sampler tray information may be used.

Line	Pos	Runs	Type	Name/Conc	ID/Action	Mass	Volume	Dil Factor
1	1		Cal	0	New Cal			
2	2		Cal	0.5	2			
3	3		Cal	1	3			
4	4		Cal	1.5	4			
5	5		Cal	2.0	5			
7	7		QC	ICB	Ignore	0	0.2	
8	8		QC	ICV1-Inorg	Ignore	1.3	1.7	
9	9		QC	ICV2-Org	Ignore	1.3	1.7	
10	10		Sample	LRB	1	1	1	1
11	11		Sample	LFB	1	1	1	1
12	12		Sample	LD1	1	1	1	1
13	13		Sample	LD2	1	1	1	1
14	14		Sample	LFM	1	1	1	1
15	15		Sample	Sample 1	1	1	1	1
				Sample n	1	1	1	1
35	35		Sample	Sample 20	1	1	1	1
36	36		QC	CCB	Ignore	0	0.2	
37	37		QC	CCV1-Inorg	Ignore	1.3	1.7	
38	38		QC	CCV2-Org	Ignore	1.3	1.7	

10.4.4 The above information can be entered in Millennium mercury software at any time.

10.5 *Transferring standards and samples auto-sampler vials for analysis;*

10.5.1 The calibration standards used to analyze the samples are digested.

10.5.2 Bring all the digested standards, blanks, and samples to room temperature.

10.5.3 Select an equilibrated calibration standard; a standard, blank, or sample for analysis.

10.5.3.1 If the selected sample is a calibration standard, transfer it

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into a calibration standard cup.

10.5.3.1.1 Place the cup into the designated calibration standard auto-sampler tray position.

10.5.3.2 If a digestion tube containing sample or standard other than a calibration standard is selected, placed the digestion tube directly in the designated auto-sampler tray position.

10.5.3.2.1 Digested samples can also be transferred from the digestion tubes into auto-sampler cups.

10.5.3.2.2 Pour approximately 20 mL of digested sample or standard into an auto-sampler sample cup.

10.5.3.2.3 Place the auto sampler cup into designated tray position.

10.5.3.2.4 This volume is not used for calculation purposes.

10.5.4 Repeat section 10.5.3 until all samples, standards, and blanks, are transferred to their proper auto-sampler tray position.

10.6 *Analyzing Calibration Standards:*

10.6.1 After the standard and sample information are entered in section 10.4, Place the reagent lines in de-ionized water container.

10.6.2 Pump de-ionized water through the system for a minimum of 3 minutes before starting analysis.

10.6.3 Transfer the reagent lines from the water in section 10.6.2 into the reagents.

10.6.4 Pump reagents through the system for a minimum of 3 minutes before starting analysis.

10.6.4.1 Analyze the calibration standards prepared in section 7.21, 7.22, and 7.26.

10.6.4.2 The instrument's computer calculates a linear regression equation and automatically prepares a standard curve by

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plotting instrument response against concentration value.

10.6.5 Evaluate the correlation coefficient of the linear regression using the Limit $r \geq 0.9975$. See section 11.2.5.1.

10.6.5.1 If the correlation coefficient (r) is less than 0.9975, verify that the standards and reagents are properly prepared and that the instrument set up is correct. Follow the trouble shooting guide provided in section 15 as necessary.

10.6.5.2 Re-analyze the calibration standards and re-evaluate r using the established limit.

10.6.5.3 If the correlation coefficient is within the limit, analyze an ICB prepared in section 7.24 and the ICV from the working control standard (WcS) prepared in section 7.28 and evaluate the results as follows;

10.6.5.3.1 ICB - Limit \leq MDL. See section 11.2.5.1.

10.6.5.3.2 ICV recovery - Limit $100 \pm 13\%$. See section 11.2.5.1.

10.6.5.4 If the ICB is outside the limit, verify that there is no contamination.

10.6.5.5 If the ICV is outside the limit of $100 \pm 13\%$, verify that the stock and dilutions for the ICV and calibration standards were properly prepared and the instrument set up and performance criteria are met. Follow the trouble shooting guide provided in section 14 or 15 as necessary.

10.6.6 The instrument is considered calibrated and standardized for this method when the correlation coefficient (r) of the linear regression is greater than or equal to 0.9975, the ICB, and ICV are within the limits.

11. SAMPLE PREPARATION AND ANALYSIS:

11.1 *Sample preparation:*

11.1.1 Create bench sheets in LIMS. Refer to Appendix 3 on page 37.

11.1.1.1 Print bench sheets (*bch_C_AIG043_Mercury_Soir.rpt*) from LIMS to record all sample preparation information.

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11.1.2 Homogenize any non-uniform samples by manual mixing.

11.1.3 Weigh between 0.1 g and 0.5 g (wet weight) of all samples including matrix duplicates and spikes and transfer them into digestion tubes. Record the weights on the LIMS Bench sheet. Place the sample tubes in digestion racks.

11.1.3.1 Perform a separate determination of percent solids using CRLSOP number AIG019.

11.1.4 Transfer 20 mL of each calibration standard into digestion tubes and place the tubes in the digestion racks. Record the volumes on the LIMS Bench sheet

11.1.5 Add 1.25 mL of nitric acid (concentrated Section.7.17) and 3.75 mL of hydrochloric acid (concentrated Section.7.4) to each digestion tubes. Cap the tubes and heat for 2 minutes in a water bath maintained at 95°C and cool.

11.1.6 Add 20 mL of reagent blank solution (section 7.22) to each sample. Record the volumes on the LIMS Bench sheet.

11.1.7 Add 15 mL of potassium permanganate (5%, Section 7.14).

11.1.8 Return the samples to the water bath maintained at 95°C for 30 minutes.

11.1.9 Add 6 mL of hydroxylamine hydrochloride prior to analysis.

11.2 ***Sample Analysis:***

11.2.1 Enter auto-sampler tray information following section 10.4 and save it.

11.2.2 Transfer samples and standards into auto sampler cups or tray for analysis following section 10.5.

11.2.3 Calibrate the instrument following section 10.6.

11.2.4 After the instrument is calibrated, sample analysis can begin.

11.2.5 Analyze Samples, ICB, ICV-CS, CCB, CCV-CS and all other audits at the required frequencies.

(See following page)

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11.2.5.1 QUALITY CONTROL SUMMARY:

AUDIT	FREQUENCY	LIMIT	ACTION
LCR	As required	$r \pm 0.9975$	Reviewed 6/23/05
DQC-BS	As required	100 \pm 10 % Target = 1.50 μ g/L	Tentative limit
QCS	As required	To pass	Reviewed 6/23/05
ICV/CCV-Inorganic)	Beginning, end of analysis and once every 20 samples	100 \pm 13 %	Reviewed 6/23/05
ICV/CCV-(Organic)	Beginning end of analysis and once every 20 samples	100 \pm 13 %	Reviewed 6/23/05
ICB/CCB	End of analysis and once every 20 samples	0 \pm 0.15 μ g/L	Reviewed 6/23/05
LRB	One Per Preparation Batch of 20 samples	0 \pm 0.15 μ g/L	Reviewed 6/23/05
LFB	One Per Preparation Batch of 20 samples	100 \pm 13 %	Reviewed 6/23/05
LD (Duplicate)	Per site or 5 % of 20 samples	$\Delta \pm 0.2 \mu$ g/L or RPD \pm 20%	Updated 6/23/05
LFM	Per site or 5 % of 20 samples	100 \pm 20%	Reviewed 6/23/05

11.2.6 All samples following a failed calibration audit must be re-analyzed after the appropriate corrective action has been successfully performed.

11.2.7 Samples exceeding the calibration range must be diluted and re-analyzed. Record the dilutions on the raw data sheet as follows;

EXAMPLE: 5/10 means that 5 mL of sample was diluted to a final volume of 10 mL. Apply the dilution factor to obtain a final concentration.

11.2.8 Samples suffering from interferences must be diluted and re-analyzed. Record the dilutions on the analysis sequence sheets as shown in section 11.2.7 and on the bench sheets. Apply the dilution factor to obtain a final sample concentration.

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11.3 *Analytical Instrument Shut Down:*

- 11.3.1 After analysis is complete, results are automatically saved.
- 11.3.2 Transfer both reagent lines to a container filled with fresh reagent water.
- 11.3.3 Pump reagent water through the system for approximately 5 to 10 minutes to clean it.
- 11.3.4 Pump air through the system for approximately 3 minutes.
- 11.3.5 Exit the Millennium mercury software. Turn off power from the instrument front then rear panel switch.
- 11.3.6 Shut off the argon gas flow at the cylinder regulator.

12. **CALCULATIONS:**

- 12.1 No additional calculations are required. The computer provides sample results directly in ug Hg/L by calculating a linear regression and applying the equations to the samples and QC standards. Information needed to calculate sample results are entered in auto-sampler tray definition section 10.4 and 10.4.3.

12.2 *Soil samples:*

- 12.2.1 The digested samples are analyzed as water samples. Refer to section 12.1 for results.
- 12.2.2 To report results on a dry weight basis, obtain the percent solids values determined in section 11.5 and section 11.5.2.1 or using CRLSOP number AIG019.
- 12.2.3 Calculate the mercury concentrations in the original soil sample on a dry weight basis as follows;

$$\text{mg/kg (dry)} = \frac{C (\mu\text{g/L}) \times V (\text{L})}{W (\text{g})} \times \frac{100}{(\% \text{ solids})}$$

Where:

- C = Concentration observed in digest ($\mu\text{g/L}$).
- V = Volume of reagent blank added in L (sec 11.1.6).
- W = Wet weight in grams.
- % solids = Obtained from a separate determination.

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13. DATA REPORTING:

- 13.1 Data are reported using LIMS (Appendix 3) to a maximum of three significant figures as follows;
 - 13.1.1 0.X, X.X, or XX.X.
- 13.2 The reporting limit for this method is 0.5 μg Hg/L. Concentrations lower than the reporting limit will be provided as requested by the customer.
- 13.3 Raw data and bench sheets are to be submitted with the data package.
- 13.4 Any irregularities in labeling or preservation of samples, or unusual observations must be documented in a case narrative and brought to the attention of the data user.
- 13.5 All electronic records associated with any data package generated must be archived following CRL.SOP GEN001.
- 13.6 All reviews are to be performed following the analytical procedure (CRL.SOP AIG044) and data review procedure (CRL.SOP GEN015).
- 13.7 Only final reports generated through LIMS are transmitted to the client. Raw data can be transmitted upon request.

14. PREVENTIVE MAINTENANCE:

- 14.1 Preventative maintenance records and log book are kept with the instrument.

15. TROUBLESHOOTING/CORRECTIVE ACTION:

- 15.1 Follow the manufactures instrument operation and software manual for system troubleshooting.
- 15.2 Filter the stannous chloride reagent used in the analysis. Check the bottom of the plastic container for precipitation. Use a new container if this occurs.
- 15.3 Document all corrective actions in the instrument log book describing the nature of the problem steps taken to resolve the problem, and final resolution.

16. REFERENCES:

- 16.1 U.S. Environmental Protection Agency, "Methods for Chemical Analysis of Water and Wastes"; EPA 600/4-79-020, Revised March 1983, Method 245.5.

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- 16.2 Millennium AAS user manual, Part# 10.045, P.S. Analytical Ltd., 2000.
- 16.3 "Element DataSystem", Ver 4.0, New User Tutorial, 1999 CequeLogic.
- 16.4 "Element DataSystem", Data Tool Ver 2.14, New User Tutorial, 1999 CequeLogic.

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APPENDIX 1

Measurement Uncertainty

Count	Date	Std. ID	Conc.	%Recovery
1	2/11/2003	DQC-LFB	1.469	97.933
2	2/11/2003	DQC-LFB	1.566	104.400
3	2/11/2003	DQC-LFB	1.522	101.467
4	2/12/2003	DQC-LFB	1.333	88.867
5	2/12/2003	DQC-LFB	1.539	102.600
6	2/12/2003	DQC-LFB	1.509	100.600
7	4/4/2003	DQC-LFB	1.706	113.733
8	4/4/2003	DQC-LFB	1.496	99.733
9	4/4/2003	DQC-LFB	1.510	100.667
10	8/13/2004	DQC-LFB	1.363	90.867
11	8/13/2004	DQC-LFB	1.473	98.200
12	8/17/2004	DQC-LFB	1.272	84.800
13	8/17/2004	DQC-LFB	1.399	93.267
14	10/6/2004	DQC-LFB	1.525	101.667
Number of replicates			14	
Amount added (µg/L)			1.500	
Mean			1.477	98.486
Standard deviation (s) µg/L)			0.1085	7.2307
Student t-value			2.145	2.145
Uncertainty			0.0622	4.1452

$$\text{Uncertainty} = st/n^{1/2}$$

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APPENDIX 2

TABLE 1: REAGENT PREPARATION BENCH SHEET:

Parameter: _____
 Reagent: _____
 LIMS ID: _____

Chemicals used	Formula	Vendor	Lot Number	Weight (g) or Volume (mL)

Final Volume: _____

Prep. Date & Analyst Initials: _____

Expiration Date: ____/____/____

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APPENDIX 3

LIMS ENTRY AND REPORTING;

1.0 CRL uses Element DataSystem (ElmNT) with Data Tool. Refer to Element DataSystem, version 4.0, New User Tutorial (CequeLogic) and Data Tool version 2.14, New User Tutorial as necessary.

1.1 *Creating a bench sheet;*

1.1.1 Create a bench sheet describing the sample preparation procedure.

1.1.2 Refer to section 9 of this SOP for general QC requirements, and section 12.6 for a summary of audit types and frequency.

1.1.3 Make sure that the preparation date in LIMS bench sheet matches the actual preparation date on the laboratory bench sheet.

Note: By convention, if sample preparation proceeds overnight, the date preparation started is used in LIMS.

1.1.4 Once all entries are complete, select DONE. ElmNT automatically create and save a file for the bench sheet.

1.2 *Data entry;*

1.2.1 Data can be entered manually or by upload using Data Tool. If results are entered manually, go to section 1.2.2. If Data Tool is used, follow the procedure given in section 1.2.3.

1.2.2 *Manual data entry:*

1.2.2.1 From the ElmNT pull down menu, select Laboratory, Data Entry/Review, and the bench sheets created in section 1.1.

1.2.2.2 Enter results in the column for **Result** in $\mu\text{g/L}$. For each result, enter the date of analysis in the column labeled **Analyzed**.

1.2.2.3 When all data are entered, click the **Save** button on the top row. After saving, proceed to the Review page by clicking **Query** on the second row. Verify that all conversions to reporting units and dilutions have been calculated correctly. Verify that reporting limits have been correctly applied. Flags may be added at this stage, following the guidance given in

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SOP GEN015. Before review by the peer, The data may be locked, and the status should be updated to Analyzed.

1.2.2.4 Follow the procedure given in section 1.3 to prepare draft or final reports.

1.2.3 *Data entry using Data Tool:*

1.2.3.1 *Creating Millennium software export files for Data Tool;*

1.2.3.1.1 A Millennium export file must first be created for use with Data Tool.

1.2.3.1.2 Create the export file in the following manner;

1.2.3.1.2.1 Turn on power to the instrument and computer. Open the Millennium Software.

1.2.3.1.2.2 Chose the Export Results function from the software and select a result **.rsf** file for export.

1.2.3.1.2.3 Save the export file as a **.csv** file to the desired drive.

1.2.3.1.2.4 The saved **.csv** file is now ready for upload using **Data Tool** with an upload file created in ElmNT. Follow the procedure given in section 1.2.3.2 to create an upload file in ElmNT.

1.2.3.2 *Creating an Upload file in ElmNT for use with Data Tool;*

1.2.3.2.1 An **Export** file must first be created in ElmNT for upload using Data Tool.

1. 2.3.2.2 From the ElmNT pull down menu, select Laboratory, Data Entry/Review, and the bench sheet created in section 1.2.

1. 2.3.2.3 Once the batch is called up in Data Entry/Review, click **Export** to create an Excel upload file in the User Directory.

1.2.3.2.3.1 Name this file in a manner that can be easily associated with that analysis.

1. 2.3.2.4 The saved upload files can now be used in Data Tool. Proceed to section 1.2.3.3 to perform upload.

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1.2.3.3 *Uploading files in Data Tool;*

- 1.2.3.3.1 Once in Data Tool, click **Browse** in the Instrument Data Files, and call up the Millennium .csv file created in 1.2.3.1.
- 1.2.3.3.2 Click **Browse** in the Element Data Entry Table, and select the upload file created in 1.2.3.2.
- 1.2.3.3.3 Select sample data files to be included in the upload by highlighting individual samples and clicking **Include**. Selected data files are shown in the lower-left hand box.
 - 1.2.3.3.3.1 If unneeded sample entries remain in the lower left-hand box, highlighting the individual samples and click **Remove** to exclude the information.
- 1.2.3.3.4 Once samples and quality controls are selected, click **Done** to return to the main Data Tool page.
- 1.2.3.3.5 From Data Tool main page, select **Merge Files**. If Unmatched Analytes or Unmatched Units appear in red, repair the cross table with the assistance, if necessary, of the Group Leader.
 - 1.2.3.3.5.1 The Millennium upload .csv file can be edited in Word Pad or excel.
- 1.2.3.3.6 Verify that the results in Initial Result are correct, and click **Save**, which will create an Excel file. Name this one differently from the name chosen in 1.2.3.2 and click **Done**.
- 1.2.3.3.7 Return to the Data Entry/Review module and click **Open**, using the .xls file created in the paragraph above. Verify that all items are correct as in the manual data entry in 1.2.2 and click **Save**. Query the data and proceed as in 1.2.2.2 and 1.2.2.3.

1.3 *Report Generation;*

1.3.1 Preparation of a draft report:

- 1.3.1.1 Ensure that all data are entered with the status of Analyzed.

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1.3.1.2 From ElmNT pull down menu, select Project Management and then Reports.

1.3.1.3 Choose the work order number, analysis, and standard report format. Choose C_Analysis.rpt format for mercury). Select Draft report.

Note: This draft report need not be signed. It is only for the purpose of review.

1.3.1.4 Submit the draft report with the data package to a peer reviewer.

1.3.1.5 After completing the data review, the peer reviewer updates the status of the LIMS entries to Reviewed.

1.3.2 Preparation of a final report:

1.3.2.1 After the peer reviewer has updated the status of the LIMS entries to Reviewed, a final report may be generated.

1.3.2.2 Ensure that all data are now in Reviewed status. Refer to section 1.3.1.2 and 1.3.1.3 of this appendix for generation of the report. Select Final Report or Modified Final Report is chosen. All pages of the report and the transmittal form must be signed and dated by the analyst.